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(54) Title: COMPOSITION FOR FORMING COATING FILMS			
(57) Abstract			
<p>A composition for forming coating films comprising: (A) a urethane (meth)acrylate obtained by reacting a polyol having 2 to 6 hydroxyl groups in a molecule, a diisocyanate, and a (meth)acrylate having a hydroxyl group; (B) a reactive diluent; and (C) fine powder of glass containing silver ion as an antibacterial agent. The composition has superior antibacterial and antifungal activities, is free from yellowing due to lights and heat, and exhibits excellent adhesion to various materials such as plastics, woods, papers, clothes, metals, and ceramics.</p>			

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COMPOSITION FOR FORMING COATING FILMS

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BACKGROUND OF THE INVENTION**Field of the Invention**

The present invention relates to a composition for forming coating films having superior antibacterial and antifungal activities, free from yellowing due to lights and heat, and exhibiting excellent adhesion to various materials such as plastics, woods, papers, clothes, metals, and ceramics.

Description of related Art

20 Resins with antibacterial characteristics (hereinafter referred from time to time to as antibacterial resins) have conventionally been manufactured by incorporating an antibacterial agent into resins. Such antibacterial resins are widely used as 25 materials for floors, furniture, toilet stool, and miscellaneous goods which are used in the places where fungi may easily be produced or the places which should be kept clean. Floors or furniture made of such an antibacterial resin may be coated with a paint. In such a 30 case, the paint is applied to the surface of the resin in which an antibacterial agent has been incorporated by kneading. As a result of covering the antibacterial resin with a paint which is not necessarily antibacterial, the surface of the floor or furniture can exhibit an 35 insufficient antibacterial effect. In the case of other products made from the antibacterial resin which does not need to be coated with a paint, the antibacterial effect

is not always required for the whole product. Some portion need to be antibacterial, but the other portion needs not be antibacterial. There are other products which are required to be antibacterial depending on the 5 application to which these products are directed. In order to respond to various requirements in these antibacterial products, two lines of products, one made from an antibacterial resin and the other made from non-antibacterial resin, must be provided. In these 10 situations, coating the floor or furniture with a paint having an antibacterial activity is more convenient.

A paint to be diluted with a solvent has been popular as the paint for coating floor and furniture in the past. The solvent, however, may vaporize and can be a 15 cause of fires, explosions, poisoning, and air pollution. In addition, the solvent used for the paint must be removed with expense of time and labor, requiring costs for securing safety of workers and heat energies for treatments. A paint cured by irradiation of ultraviolet 20 light or electron beam without using any solvent (non-solvent type paint) has therefore been used in recent years.

More recently, development of a coating material cured by UV light or electron beam containing an 25 antibacterial agent is contemplated. For example, Japanese Patent Application Laid-Open (kokai) No. 164368/1990 discloses an electron beam-curable type coating agent containing a metal-containing antibacterial agent. Japanese Patent Application Laid-Open (kokai) No. 30 107972/1994 discloses a UV-curable type paint composition which contains fine particles of antibacterial or antifungal inorganic gel containing silver ion. These compositions exhibit an antibacterial activity against microorganisms such as E-coli and staphylococcus aureus.

Growth of mold such as black mold and blue mold, however, cannot be effectively suppressed by merely adding conventional inorganic-type antibacterial agents to UV-curable resins. In addition, this type of 5 antibacterial agents cause the resin to be colored yellow by heat or light. This yellowing of resin is thought to be caused by the reduction of silver ion in the inorganic substance into metallic silver due to heat or light.

Japanese Patent Application Laid-Open (kokai) No. 10 291654/1995 discloses an antibacterial glass powder which is difficult to get colored. This laid-open patent, however, merely proposes the addition of the antibacterial glass powder to organic or inorganic materials, but does not disclose the antibacterial or antifungal activity of 15 this glass powder, the composition for exhibiting film forming characteristics using this glass fiber, and improvement in the adhesion property to other materials such as plastics, woods, clothes, metals, and ceramics.

20

SUMMARY OF THE INVENTION

An object of the present invention is therefore to solve the above problems and provide a composition for forming coating films possessing superior antibacterial or antifungal activity, free from yellowing due to light and 25 heat, and exhibiting excellent adhesion to other materials such as plastics, woods, clothes, metals, and ceramics.

This object has been achieved by the present invention by a composition for forming coating films comprising:

30 (A) a urethane (meth)acrylate obtained by reacting a polyol having 2 to 6 hydroxyl groups in a molecule, a diisocyanate, and a (meth)acrylate having a hydroxyl group;
(B) a reactive diluent; and

(C) fine powder of glass containing silver ion as an antibacterial agent.

In a preferred embodiment of the present invention, said composition further comprises one or more 5 components selected from (D) a radiation polymerization initiator, (E) an antibacterial agent other than the component (C), and (F) an ultraviolet absorber.

The invention furthermore relates to cured coatings obtained by radiation curing of said coatings.

10

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

Each component for the composition of the present invention will be illustrated in detail.

15

(A) Urethane (meth)acrylate

The urethane (meth)acrylate used in the composition of the present invention as the component (A) can be obtained by reacting (a) a polyol having 2 to 6 20 hydroxyl groups in a molecule, (b) a diisocyanate, and (c) a (meth)acrylate having a hydroxyl group.

A polyether polyol, a polyester polyol, a polycarbonate polyol, or a polycaprolactone polyol may be used as the component (a), which is the polyol having 2 to 25 6 hydroxyl groups in a molecule. These polyols may be used either individually or in combination of two or more. The manner of polymerization of each constitutional unit in these polyols is not specifically limited and may be random polymerization, block polymerization, or graft 30 polymerization.

Aliphatic polyether polyols, alicyclic polyether polyols, and aromatic polyether polyols are given as the polyether polyols.

Included in the specific examples of the

aliphatic polyether polyols are polyhydric alcohols, such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, 5 ethylene oxide addition triol of trimethylolpropane, propylene oxide addition triol of trimethylolpropane, ethylene oxide-propylene oxide addition triol of trimethylolpropane, dipentaerythritol, ethylene oxide addition tetraol of pentaerythritol, and ethylene oxide addition hexaol of dipentaerythritol; and polyether polyols obtained by the ring-opening copolymerization of two or more ionic-polymerizable cyclic compounds. Examples of the ionic-polymerizable cyclic compound include cyclic ethers such as ethylene oxide, propylene 10 oxide, butene-1-oxide, isobutene oxide, 15 3,3-bischloromethyloxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrine, glycidyl methacrylate, allyl glycidyl 20 ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidyl benzoate. Specific 25 combinations of two or more of these ionic-polymerizable cyclic compounds include the combinations of tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyltetrahydrofuran, tetrahydrofuran and ethylene oxide, propylene oxide and ethylene oxide, ethylene oxide and butene-1-oxide, and tetrahydrofuran and butene-1-oxide. It is also possible to use a polyether 30 polyol obtained by the ring-opening copolymerization of one of the above-mentioned ionic-polymerizable cyclic compounds and a cyclic imine such as ethylene imine, a

cyclic lactone such as β -propiolactone and glycolic acid lactide, or a dimethylcyclopolysiloxane.

Given as examples of the alicyclic polyether polyol are alkylene oxide addition diol of hydrogenated bisphenol A, alkylene oxide addition diol of hydrogenated bisphenol F, and alkylene oxide addition diol of 1,4-cyclohexane diol.

As examples of the aromatic polyether polyol are alkylene oxide addition diol of bisphenol A, alkylene oxide addition diol of bisphenol F, alkylene oxide addition diol of hydroquinone, alkylene oxide addition diol of naphthohydroquinone, and alkylene oxide addition diol of anthrahydroquinone.

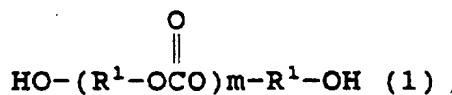
These polyether polyols are commercially available. Commercially available aliphatic polyether polyols include PTMG1000(tm) and PTMG2000(tm) (Mitsubishi Chemical Co., Ltd.); PPG1000(tm), EXCENOL 4020(tm), EXCENOL 3020(tm), EXCENOL 2020(tm), EXCENOL 1020(tm) (Asahi Glass); PEG1000(tm), UNISAFE DC1100(tm), UNISAFE 20 DC1800(tm), UNISAFE DCB1100(tm), UNISAFE DCB1800(tm) (Nippon Oil and Fats Co., Ltd.); PPTG4000(tm), PPTG2000(tm), PPTG1000(tm), PTG2000(tm), PTG3000(tm), PTG650(tm), PTG400(tm), PTGL2000(tm), PTGL1000(tm) (Hodogaya Chemical Co., Ltd.); Z-3001-4(tm), Z-3001-5(tm), PBG2000A(tm), PBG2000B(tm) (Daiichi Kogyo Seiyaku Co., Ltd.); TMP30(tm), PNT4 Glycol(tm), EDA P4(tm), EDA P8(tm) (Nippon Emulsion Co., Ltd.); Quadrol(tm) (Asahi Denka Kogyo); and Tone Polyol 0200(tm), Tone Polyol 0221(tm), Tone Polyol 0301(tm), Tone Polyol 0310(tm), Tone Polyol 2201(tm), Tone Polyol 2221(tm) (Union Carbide Corp.).

Given as examples of commercially available aromatic polyether polyols are UNIOL DA400(tm), UNIOL DA700(tm), UNIOL DA1000(tm), and UNIOL DB400(tm) (Nippon Oil and Fats Co., Ltd.).

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The polyester polyols can be obtained, for example, by reacting a polyhydric alcohol and a polybasic acid. Here, given as specific examples of the polyhydric alcohol are ethylene glycol, polyethylene glycol, 5 propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,4-butene diol, 1,5-pentane diol, 1,6-hexane diol, 1,7-heptane diol, 1,8-octane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, 1,2-bis(hydroxyethyl)cyclohexane, 10 2,2-diethyl-1,3-propane diol, 3-methyl-1,5-pentane diol, 1,9-nonane diol, 2-methyl-1,8-octane diol, glycerin, trimethylolpropane, ethylene oxide addition compound of trimethylolpropane, propylene oxide addition compound of trimethylolpropane, ethylene oxide-propylene oxide 15 addition compound of trimethylolpropane, sorbitol, pentaerythritol, dipentaerythritol, alkylene oxide addition polyols, such as TMP30(tm), PNT4 Glycol(tm), EDA P4(tm), EDA P8(tm) (Nippon Emulsion Co., Ltd.); Quadrol(tm) (Asahi Denka Kogyo); and Tone Polyol 0200(tm), 20 Tone Polyol 0221(tm), Tone Polyol 0301(tm), Tone Polyol 0310(tm), Tone Polyol 2201(tm), Tone Polyol 2221(tm) (Union Carbide Corp.). Specific examples of the polybasic acid include phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, and sebacic 25 acid. Commercially available product of these polyester polyols include, for example, Korapole P-2010(tm), PMIPA(tm), PKA-A(tm), PKA-A2(tm), and PNA-2000(tm) (Kuraray Co.).

As examples of the polycarbonate polyol, 30 polycarbonate diols represented by the following formula (1) can be given.



(In the formula (1), R¹ is an alkylene group having 2 to 20 carbon atoms, a (poly)ethyl ne glycol residue, a (poly)propylene glycol residue, or a (poly)tetramethylene glycol residue, and m is an integer of 1 to 10.)

Given as specific examples of R¹ are residues of the group such as 1,4-butane diol, 1,5-pentane diol, neopentyl glycol, 1,6-hexane diol, 1,4-cyclohexane dimethanol, 1,7-heptane diol, 1,8-octane diol, 1,9-nonane diol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, and tetrapropylene glycol. Included in commercially available polycarbonate polyols are DN-980(tm), DN-981(tm), DN-982(tm), DN-983(tm) (Nihon Polyurethane); PC-8000(tm) (PPG); and PNOC1000(tm), PNOC2000(tm), PMC100(tm), PMC2000(tm) (Kuraray Co.); CD-205(tm), CD-208(tm), CD-210(tm), CD-220(tm), CD-205PL(tm), CD-208PL(tm), CD-210PL(tm), CD-220PL(tm), CD-205HL(tm), CD-208HL(tm), CD-210HL(tm), CD-220HL(tm), CD-210T(tm), and CD-221T(tm) (BASF).

Given as examples of the polycaprolactone polyols are polycaprolactone diols obtained by the addition reaction of ϵ -caprolactone and a diol such as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, or 1,4-butane diol. These polycaprolactone diols can also be commercially available under the trademarks such as PLACCEL(tm) 205, 205AL, 212, 212AL, 220, 220AL (Daicell Co., Ltd.).

Further, given as examples of polyols other than those enumerated above are ethylene glycol, propylene glycol, tetramethylene glycol, 1,4-butene diol, 1,5-pentane diol, 1,6-hexane diol, 1,7-heptane diol,

1,8-octane diol, neopentyl glycol, 1,4-cyclohexane diol,
1,4-cyclohexane dimethanol,
1,2-bis(hydroxyethyl)cyclohexane, 2,2-diethyl-1,3-propane
diol, 3-methyl-1,5-pentane diol, 1,9-nonane diol,
5 2-methyl-1,8-octane diol, glycerin, dimethylol compound of
dicyclopentadiene, tricyclodecane dimethanol,
poly- β -methyl- δ -valerolactone diol, polybutadiene with
terminal hydroxy groups, hydrogenated polybutadiene with
terminal hydroxy groups, castor oil-denatured diol,
10 polydimethylsiloxane with terminal diols, and
polydimethylsiloxane carbitol-denatured diols,
trimethylolpropane, sorbitol, and pentaerythritol.

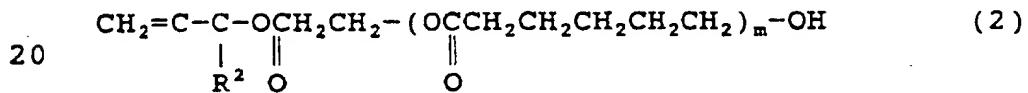
Among these polyols, polyether polyols and
polycarbonate polyols are preferred, with particularly
15 preferred being the ethylene oxide addition triol of
trimethylolpropane.

The number average molecular weight of the
polyols (a) is in the range of 50 to 15,000, and
preferably 100 to 8,000.

20 Given as examples of the diisocyanate (b) are
2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate,
1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate,
1,5-naphthalene diisocyanate, m-phenylene diisocyanate,
p-phenylene diisocyanate,
25 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate,
4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene
diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane
diisocyanate, isophorone diisocyanate,
2,2,4-trimethylhexamethylene diisocyanate,
30 bis(2-isocyanate-ethyl)fumarate, 6-isopropyl-1,3-phenyl
diisocyanate, 4-diphenylpropane diisocyanate, lysine
diisocyanate, hydrogenated diphenylmethane diisocyanate,
hydrogenated xylylene diisocyanate, and
tetramethylxylylene diisocyanate. Among these

diisocyanates, particularly preferred are hydrogenated xylylene diisocyanate, isophorone diisocyanate, and hydrogenated diphenylmethane diisocyanate. These diisocyanates may be used either individually or in 5 combination of two or more.

Examples of the (meth)acrylate having a hydroxyl group (c) include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl 10 (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxyalkyl(meth)acryloyl phosphate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane 15 di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, and (meth)acrylates represented by the following formula (2),



wherein R^2 is a hydrogen atom or a methyl group and m denotes an integer of 1 to 15, preferably 1 to 4.

25 In addition, compounds obtained by an addition reaction between compounds containing a glycidyl group, such as, alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and (meth)acrylic acid can also be used. Among these (meth)acrylates having a hydroxyl 30 group, particularly preferred are 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, and 2-hydroxybutyl (meth)acrylate.

There are no specific limitations to the method for synthesizing the urethane (meth)acrylate. The 35 following methods (i) to (iii) can be given as examples.

(i) A method of reacting the polyisocyanate (b) and the (meth)acrylate having a hydroxyl group (c), and then reacting the polyol (a).

5 (ii) A method of reacting the polyol (a), the polyisocyanate (b), and the (meth)acrylate having a hydroxyl group (c) altogether.

(iii) A method of reacting the polyol (a) and the polyisocyanate (b), and then reacting the (meth)acrylate having a hydroxyl group (c).

10 When the average hydroxyl group content in one mol of polyol is n , the proportion of both the diisocyanate and the (meth)acrylate having a hydroxyl group for one mol of the polyol is n to $n+1$ mols.

15 In the reaction for producing the urethane (meth)acrylate of the present invention, a urethanization catalyst such as copper naphthenate, cobalt naphthenate, zinc naphthenate, n-butyl-tin-laurylate, triethylamine, 1,4-diazabicyclo[2.2.2]octane, or 1,4-daza-2-methylbicyclo[2.2.2]octane is used, generally, 20 in an amount of 0.01 to 1 part by weight for 100 parts by weight of the reaction raw materials. The reaction temperature is normally in the range of 0-90°C, and preferably 10-80°C.

25 The urethane (meth)acrylate used in the present invention has a weight average molecular weight of 400 to 20,000, and preferably 600 to 10,000.

30 The urethane (meth)acrylate is incorporated in the composition of the present invention in an amount of 5 to 60% by weight. If the amount of the urethane (meth)acrylate is less than 5% by weight, coating films covering surfaces of various materials may have only poor flexibility and adhesion characteristics. If more than 60% by weight, the viscosity of the composition may be so great that it is difficult to obtain uniform coatings on

the surfaces of various materials. In addition, too great an amount of the urethane (meth)acrylate makes soft coatings which are easily damaged.

(B) Reactive diluent

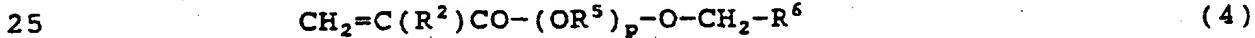
5 The component (B), the reactive diluent, can be a (meth)acrylate compound having at least one (meth)acryloyl group in the molecule, either mono-functional compounds having one (meth)acryloyl group or poly-functional compounds having two or more 10 (meth)acryloyl groups or a compound having one or more vinyl groups such as vinyl ether or N-vinyl groups. The reactive diluents can be used at a suitable proportion.

15 Enumerated as examples of the monofunctional compounds are 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl 20 (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, isoctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl 25 (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, octadecyl (meth)acrylate, stearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl (meth)acrylate, cyclohexyl 30 (meth)acrylate, phenoxyethyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, ethoxyethoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate,

methoxypolypropylene glycol (meth)acrylate,
dicyclopentadienyl (meth)acrylate, dicyclopentanyl
(meth)acrylate, dicyclopentenyl (meth)acrylate,
tricyclodecanyl (meth)acrylate, isobornyl (meth)acrylate,
5 bornyl (meth)acrylate, dimethylaminoethyl (meth)acrylate,
diethylaminoethyl (meth)acrylate,
7-amino-3,7-dimethyloctyl (meth)acrylate, (meth)acryloyl
morpholine,
2-(meth)acryloyloxyethylphthalic acid,
10 2-(meth)acryloyloxyethylhexahydrophthalic acid,
2-(meth)acryloyloxypropylphthalic acid,
2-(meth)acryloyloxypropyltetrahydrophthalic acid,
2-(meth)acryloyloxypropylhexahydrophthalic acid,
2-(meth)acryloyloxyethylsuccinic acid, and compounds
15 represented by the following formulas (3) to (6).



wherein R² is a hydrogen atom or a methyl group, R³ is an alkylene group having 2 to 6, preferably 2 to 4, carbon atoms, R⁴ is a hydrogen atom or an alkyl group having 1 to 12, preferably 1 to 9, carbon atoms, and m is an integer from 1 to 12, preferably 1 to 8;



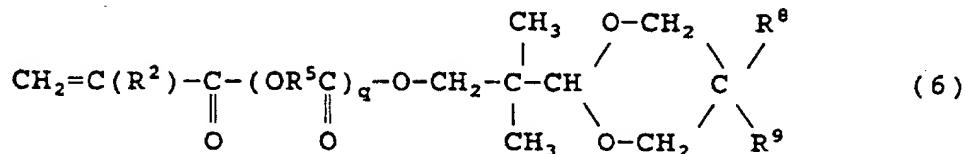
wherein R² has the same meaning as defined for formula (3), R⁵ is an alkylene group having 2 to 8, preferably 2 to 5, carbon atoms; R⁶ is a tetrahydrofuryl group, and p is an integer from 1 to 8, preferably 1 to 4;



where in R^2 , R^5 , and p have the same meanings as defined

above, R⁷ is a phenyl group, optionally substituted with an alkyl group having 1 to 12, preferably 1 to 9, carbon atoms; and

5



10

wherein R² and R⁵ have the above defined meaning and q is an integer from 0 to 8; and R⁸ and R⁹ are individually a hydrogen atom, an alkyl group containing 1 to 6 carbon atoms, a group -R¹⁰-A, wherein R¹⁰ is an alkylene group containing 1 to 6 carbon atoms and A is a (meth)acryloyloxy group.

Examples of suitable vinyl group-containing monomers such as N-vinyl pyrrolidone, N-vinyl caprolactam, vinyl imidazole, vinyl pyridine, hydroxy butyl vinyl ether, lauryl vinyl ether, cetyl vinyl ether, 2-ethylhexyl vinyl ether, and N-vinyl carbazole.

Commercially available monofunctional compounds include ARONIX(tm) M101, M102, M111, M113, M114, M117, M-5300, M-5400, M-5500, M-5600 (Toagosei Chemical Industry Co., Ltd.); KAYARAD(tm) TC110S, R629, R644 (Nippon Kayaku Co., Ltd.); Viscoat(tm) LA, STA, IBXA, DMA, 158, 190, 192, 2000, 2100, 2150, 2180, 3700 (Osaka Organic Chemical Industry, Ltd.); NK Ester(tm) SA, A-SA (Shin-Nakamura Chemical Co.); and Lightacrylate(tm) L-A, S-A, BO-A, EC-A, DPM-A, Lightester(tm) PA (Kyoeisha Chemical Co.).

Examples of the polyfunctional compounds include: ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol

di(meth)acrylate, polyethylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, hydroxypivalic acid
5 neopentyl glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, trimethylolpropanetrioxethyl (meth)acrylate,
10 trimethylolpropanetrioxypropyl (meth)acrylate, trimethylolpropanepolyoxyethyl (meth)acrylate, trimethylolpropanepolyoxypropyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate,
15 di(meth)acrylate of ethylene oxide addition bisphenol A, di(meth)acrylate of ethylene oxide addition bisphenol F, di(meth)acrylate of propylene oxide addition bisphenol A, di(meth)acrylate of propylene oxide addition bisphenol F, tricyclodecanedimethanol di(meth)acrylate, bisphenol A
20 epoxy (meth)acrylate, and bisphenol F epoxy (meth)acrylate.

Given as commercially available polyfunctional compounds are YUPIMER-UV(tm), SA1002(tm), SA2007(tm) (Mitsubishi Chemical Co., Ltd.), Viscoat(tm) 195, 215, 25 230, 260, 295, 300, 310, 312, 360, 400, 700, GPT (Osaka Organic Chemical Industry Ltd.), KAYARAD MANDA(tm), DP_{HA}, R-604, DPCA-20, DPCA-30, DPCA-60, DPCA-120, HX-620, D-310, D-330 (Nippon Kayaku Co., Ltd.), and ARONIX(tm) M-210, M-215, M-220, M-270, M-310, M-315, M-325, M-350, M-360, 30 M-400, M-450, M-6100, M-6500, M-7100, M-8030, M-8530 (Toagosei Chemical Industry Co., Ltd.); and SR-355(tm) (Satomer Co.).

These reactive diluents, preferably comprising at least one (meth)acrylate compound; are preferably

incorporated into the composition of the present invention in an amount of 30 to 90% by weight.

(C) Inorganic antibacterial agent

5 The inorganic antibacterial agent used as the component (C) in the composition of the present invention is a fine powder of glass containing silver ions. Specific examples are inorganic glass such as silicate glass, soda lime glass, borosilicate glass, or 10 phosphosilicate glass, all containing silver ion as an essential component. The amount of the silver ion contained in these inorganic antibacterial agents is normally 0.001 to 10% by weight, and preferably 0.01 to 5% by weight. If less than 0.001% by weight, the 15 antibacterial effect is insufficient. It is difficult for glass to contain 10% by weight or more of silver ion in a stable manner, and such a glass can be manufactured only with difficulty.

These inorganic antibacterial agents comprising 20 silver ion-containing glass may contain inorganic ions other than silver ion, such as copper ion, zinc ion, lead ion, tin ion, cadmium ion, calcium ion, magnesium ion, barium ion, bismuth ion, aluminum ion, germanium ion, lithium ion, sodium ion, potassium ion, cobalt ion, 25 titanium ion, arsenic ion, antimony ion, and zirconium ion. Of these, copper ion, zinc ion, calcium ion, magnesium ion, aluminum ion, sodium ion, potassium ion, cobalt ion, and titanium ion are preferred.

Commercially available inorganic antibacterial 30 agents of this type include, for example, antibacterial biocomposite glass fine powder manufactured by Koa Glass Co., Ltd. and IonPure(tm), WPA(tm), and IP(tm), all manufactured by Ishizuka Glass Co., Ltd.

These inorganic antibacterial agents may be used

either individually or in combination of two or more, and incorporated in the composition of the present invention in an amount of 0.1 to 10% by weight, and preferably 0.5 to 5% by weight. If the amount of the inorganic 5 antibacterial agents is less than 0.1% by weight, the composition may not exhibit sufficient antibacterial activity. If more than 10% by weight, light resistance of the composition may be impaired.

These antibacterial agents are used in the form 10 of fine powder dispersed in the composition. The mean particle size of the fine powder is usually less than 50 μm , and preferably less than 20 μm .

Other components

15 It is desirable that the composition of the present invention contains a radiation polymerization initiator as a component (D). Radiation in this invention means infrared rays, visible lights, ultraviolet lights, X-rays, electron beam, α -rays, β -rays, γ -rays, and the 20 like.

Examples of the radiation polymerization initiators are benzophenone, benzoine ethyl ether, benzoine propyl ether, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, 3-methylacetophenone, 25 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one, 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone, 30 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, and 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, methylbenzoylformate, xanthone, fluorenone,

benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, thioxanthone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, oligo[2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl)propan 5 one].

The radiation polymerization initiator can be commercially available under the trademarks of IRGACURE^(tm) 184, 261, 369, 500, 651, 907 (manufactured by Ciba Geigy); Lucirine LR8728^(tm) (manufactured by BASF); 10 Darocur^(tm) 953, 1116, 1173, 1664, 2273, 2959, ZL1, 3331 (manufactured by Merck Co.); Uvecryl P36^(tm) (manufactured by UCB Co.); VICURE 55^(tm) (manufactured by AKZO Co.); and ESACURE^(tm) KIP100F and KIP150 (manufactured by Lamberti Co.).

15 Among these radiation polymerization initiators, particularly preferred are benzophenone, IRUGACURE^(tm) 184, VICURE 55^(tm), ESACURE^(tm) KIP100F, ESACURE^(tm) KIP150, and Darocur^(tm) 1173.

These radiation polymerization initiators may be 20 used either individually or in combination of two or more, and incorporated in an amount less than 10% by weight, preferably 1 to 10% by weight, in the composition of the present invention.

An antibacterial agent other than the 25 above-described inorganic antibacterial agent (C) can be incorporated in the composition of the present invention as component (E). This component (E) is not specifically limited so long as the component exhibits an antibacterial or antifungal activity. Coatings with a more excellent 30 antifungal effect can be obtained by incorporating the component (E) as compared with the composition containing only the component (C). Either an organic or inorganic antibacterial agent can be used as the component (E).

Given as examples of the inorganic antibacterial

agents used as the component (E) are fine powder of metal oxide such as zinc oxide and titanium oxide; metal alloys containing metals such as Co and Cu; and metal ions such as silver ion, copper ion, zinc ion, calcium ion, 5 magnesium ion, aluminum ion, sodium ion, potassium ion, cobalt ion, or titanium ion carried on an inorganic compound such as zeolite, silica gel, alumina, apatite, titania, zirconium phosphate, calcium hydroxide, or magnesium hydroxide. Examples of these antibacterial 10 agents which are commercially available include Zeomic(tm) (manufactured by Shinanen Zeomic Co.) produced by replacing the sodium ion in porous synthetic zeolite with an antibacterial ions such as silver ion, copper ion, or zinc ion; Bactekiller(tm) (manufactured by Kanebo Co., 15 Ltd.) which is an alminosilicate-type synthetic zeolite carrying silver ion or copper ion; AIS(tm) (manufactured by Shokubai Kasei Co.) which is magnesium alminosilicate carrying silver ion, copper ion, or zinc ion; Apatizer A(tm), Apatizer AW(tm), Apatizer A25(tm), Apatizer NB(tm) 20 (manufactured by Sangi Co.) which are apatite (calcium phosphate) to which an antibacterial ion such as silver ion or zinc ion has been immobilized by adsorption; RAP(tm) (manufactured by Rasa Industry Co., Ltd.) which is aluminum polyphosphate carrying silver ion, copper ion, or 25 zinc ion; Amenitop(tm) (manufactured by Matsushita Electric Co., Ltd.) which is silica gel carrying thiophosphate silver complex; Rentoba(tm) (manufactured by Rengo Co., Ltd.) which is calcium silicate carrying silver ion; Novalon(tm) (manufactured by Toagosei Chemical 30 Industry, Ltd.) which is zirconium phosphate carrying silver ion; SEABIO(tm) (manufactured by Sea Water Chemical Research Institute) which is calcium hydroxide or magnesium hydroxide carrying zinc ion or copper ion; and Silver Ace(tm) (manufactured by Taihei Chemical Industry,

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Ltd.) which is scarcely soluble phosphate carrying silver ion.

Examples of the organic antibacterial agents used as the component (E) are: quaternary ammonium salts 5 represented by the following formulas (7) or (8),



wherein R^9 , R^{10} , R^{11} , and R^{12} are individually an organic 10 group consisting of 1 to 30 carbon atoms, 3 to 62 hydrogen atoms, 0 to 15 oxygen atoms, 0 to 5 nitrogen atoms, 0 to 3 silicon atoms, and 0 to 3 sulfur atoms, such as an alkyl group having 1 to 18 carbon atoms which may be substituted, a phenyl group, a substituted phenyl group 15 with at least one C_1 to C_6 alkyl substituent, a naphthyl group, an amide bond-containing group of the formula $-R^{13}CONHR^{14}-$ (wherein R^{13} is an alkyl group having 1 to 18 carbon atoms or a phenyl group and R^{14} represents an alkylene group having 1 to 8 carbon atoms), a 20 trimethoxysilylalkyl group, a dimethoxysilylalkyl group, or a monomethoxysilylalkyl group, and X represents Cl , Br , I , HSO_4 , or CH_3SO_4 ;



wherein P^+ is a pyridinium group or a quinolinium group, 25 R^{15} is an alkyl group having 1 to 18 carbon atoms which links to the nitrogen atom of the pyridinium group or the quinolinium group, and X represents Cl , Br , I , HSO_4 , or CH_3SO_4 ; amphoteric surfactants such as carboxy betaine, 30 sulfo betaine, aminocarboxylic acid, imidazolinium betaine, and lecithin; phenols such as phenol, catechol, resorcinol, cresol, 3,5-xylenol, pyrogallol, thymol, 2-benzyl-4-chlorophenol, 3-methyl-4-chlorophenol,

(2,2'-dihydroxy-5,5'-dichloro)-diphenylmethane,
2-hydroxyphenyl-2',4'-dichlorobenzyl ether,
2-phenylphenol, α -naphthol, and β -naphthol; imidazole
derivatives such as 2-(5'-aminopentyl)benzimidazole,
5 2-methoxycarbonylaminobenzimidazole,
2-(4-thiazolyl)-benzimidazole, and methyl
benzimidazolylcarbamate; triazole derivatives such as
2-thiocyanato-methylthiobenzthiazole, benzotriazole,
tolyltriazole, and
10 α -[2-(4-chlorophenyl)-ethyl]- α -(1,1-dimethylethyl)-1H-1,2,
4-triazol-1-yl-ethanol; guanidine derivatives such as
chlorohexadine and polyhexamethylene biguanidine
hydrochloride; zinc pyrithione, allyl isothiocyanate,
 β -thujaplicin, chitosan, and polylysine.

15 Commercially available products of these organic
antibacterial agents are Preventol(tm) A2, A2-D, A3, A4-S,
A5, A6, A7-D, A8, AS2, B2, BCM, BP, CMK, CMK-Na, CR, D2,
D3, D4, D5, D6, D7, GD, O-Extra, O-N-Extra, OF, R80, R50,
SB, WB, Z, CI3, CI4, CI5, CI6, CI7-100, CI8-100,
20 Soblol(tm) A, A-Na, M, M-Na, P, P-Na, Bercoline(tm)
(products of Bayer), Biocut(tm) KGS, AF40, N, SK, BM30,
BM100, TR120, AG, MT, ZP, DC100, SP100, TS, 2210,
Millcut(tm) 90 and 88A (products of Dainippon Ink and
Chemicals, Inc.).

25 Among the above antibacterial agents, organic
antibacterial agents are preferred. Particularly
preferred among the organic antibacterial agents are
benzotriazole, tolyltriazole,
 α -[2-(4-chlorophenyl)-ethyl]- α -(1,1-dimethylethyl)-1H-1,2,
30 4-triazol-1-yl-ethanol, Biocut(tm) 210, and Preventol(tm)
A8.

The antifungal activity of the composition can
be improved by adding these organic antibacterial agents.
The antibacterial agents of component (E) can be used

either individually or in combination of two or more, and can be incorporated into the composition of the present invention in an amount of less than 5% by weight, preferably 0.1 to 3% by weight, and particularly 5 preferably 0.2 to 2% by weight. If incorporated more than 5% by weight, light resistance of the resulting composition is impaired.

The composition of the present invention may contain a UV absorber as component (F). Examples of the 10 UV absorbers include Tinuvin(tm) P, 213, 234, 320, 326, 327, 328, 329, 400 (Ciba Geigy); Seesorb(tm) 102, 103, 202, 501, 712 (manufactured by Shypro Kasei Kaisha, Ltd.); and Needral(tm) W-100, U-100 (Taki Chemical Co.). The 15 component (F) can be incorporated into the composition of the present invention in an amount of less than 5% by weight, preferably 0.1 to 3% by weight, and particularly preferably 0.2 to 2% by weight. The incorporation of the component (F) in the amount of 0.2 to 2% by weight can improve light resistance of the resulting composition 20 without unduly impairing the curing rate.

A photo-sensitizer may be used, if necessary. Given as examples of the photo-sensitizer are triethylamine, diethylamine, N-methyldiethanolamine, ethanolamine, 4-dimethylaminobenzoic acid, ethyl 25 4-dimethylaminobenzoate, isoamyl 4-dimethylaminobenzoate, and commercially available products such as Uvecryl(tm) P102, P103, P104, and P105 (manufactured by UCB Co). The photo-sensitizers are added in an amount of 0 to 5 parts by weight for 100 parts by weight of the composition of 30 the present invention.

Beside the components (A), (B), (C), (D), (E), and (F), radical polymerizable compounds other than acryl or vinyl group-containing compounds as defined under (B) may be incorporated into the composition of the present

invention. Vinyl acetate, vinyl propionate, maleic acid anhydride, itaconic acid, fumaric acid, styrene, divinylbenzene, and unsaturated polyesters are given as examples of such compounds. The unsaturated polyesters 5 are esters of a dicarboxylic acid having a radical polymerizable double bond and an alcohol. Maleic acid anhydride, itaconic acid, and fumaric acid are given as examples of the dicarboxylic acid having a radical polymerizable double bond. Given as examples of the 10 alcohol are monohydric alcohols such as methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butyl alcohol, iso-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, n-hexanol, cyclohexanol, and 2-ethylhexyl alcohol; (poly)ethylene glycols such as ethylene glycol, diethylene 15 glycol, and triethylene glycol; (poly)propylene glycols such as propylene glycol, dipropylene glycol, and tripropylene glycol; dihydric alcohol such as 1,6-hexane diol; and trihydric alcohols such as glycerine and trimethylol propane.

20 Further, added to the composition of the present invention as other additives are epoxy resin, polyamide, polyamideimide, polyurethane, polybutadiene, chloroprene, polyether, polyester, pentadiene derivatives, SBS (styrene/butadiene/styrene block copolymer), hydrogenated SBS, SIS (styrene/isoprene/styrene block copolymer), petroleum resin, xylene resin, ketone resin, fluorine-containing oligomer, silicon-containing oligomer, polysulfide-type oligomer, and the like.

25 Beside the above components, the composition of the present invention may be formulated with various components, as required, such as antioxidants, photo-stabilizers, silane coupling agents, antifoaming agents, leveling agents, slipping agents, flattening agents, antistatic agents, surfactants, preservatives, thermal

polymerization inhibitors, plasticizers, lubricants, solvents, fillers, coloring agents, wettability improvers, and coated surface improvers. Specific examples of antioxidants which can be used are Irganox(tm) 245, 259, 5 565, 1010, 1035, 1076, 1081, 1098, 1222, 1330 (Ciba Geigy). The antioxidants can be used in an amount less than 2 % by weight of the composition of the present invention. As photo-stabilizers Tinuvin(tm) 144, 292, 622LD (Ciba Geigy), Sanol LS440, LS770 (Sankyo Chemical 10 Co.), and Sumisorb(tm) TM-061 (manufactured by Sumitomo Chemical Industries) can be given as examples. The photo-stabilizers can be used in an amount less than 5 % by weight of the composition of the present invention.

Examples of silane coupling agents which can be 15 given are γ -aminopropyltriethoxy silane, γ -mercaptopropyltri-methoxy silane, γ -methacryloxypropyltrimethoxy silane, and commercial products such as SH6062(tm), SH6030(tm) (Toray Silicone Co.) and KBE403(tm), KBE603(tm), KBE903(tm) (Shin-Etsu 20 Chemical Co.). The silane coupling agents can be added in an amount less than 2 parts by weight for 100 parts by weight of the composition of the present invention. Given as examples of the antifoaming agents are organic copolymers which do not contain a silicon atom or a 25 fluorine atom such as Florene(tm) AC-202, AC-300, AC-303, AC-326F, AC-900, AC-1190, AC-2000 (Kyoelisha Chemical Co.); silicon-type antifoaming agents such as Florene(tm) AC-901, AC-950, AC-1140, AO-3, AO-40H (Kyoelisha Chemical Co.) and FS1265(tm), SH200(tm), SC5550(tm), SC5540(tm), 30 SC5570(tm), F-1(tm), SD5590(tm) (Toray Silicone Co.); and fluorine-containing antifoaming agents such as Megafac(tm) F-142D, F-144D, F-178K, F-179, F-815 (Dainippon Ink and Chemicals, Inc.). The antifoaming agents can be added in an amount less than 1 part by weight for 100 parts by

weight of the composition of the present invention. Polyflow(tm) No. 7, No. 38, No. 50E, S, 75, No. 75, No. 77, No. 90, No. 95, No. 300, No. 460, ATF, KL-425 (Kyoeisha Chemical Co.) are given as examples of the 5 leveling agents. The leveling agents can be added in an amount less than 2 parts by weight for 100 parts by weight of the composition of the present invention. Granol(tm) 100, 115, 200, 400, 410, 440, B-1484 (Kyoeisha Chemical Co.) are given as examples of the slipping agents. The 10 slipping agents can be added in an amount less than 2 % parts by weight for 100 parts by weight of the composition of the present invention. Given as examples of the glossing preventives are inorganic glossing preventives such as wet silica, dry silica, magnesium carbonate, and 15 talc, and organic glossing preventives such as fine particles of polyethylene, polypropylene, polyurethane, poly(methyl methacrylate), polycarbonate, urea-formaldehyde resin, benzoguanamine-formaldehyde resin, melamine-formaldehyde resin, and polytetrafluoroethylene. Commercially available products 20 of the glossing preventives include TS-100(tm), HK-125(tm), HK-400(tm), VPA5F(tm), OK412(tm), OK500(tm), OK520(tm) (Degussa Japan), AEROSIL(tm) 200, T600 (Japan Aerosil Co.), Nipseal(tm) E150K, E170, E200, E22, OA, 25 SS-10, SS-15, SS-10A, SS-20, SS-30P, SS-40, SS-50, SS-60, SS-70, SS-100 (Nippon Silica Co.), X-80(tm) (Tokuyama Soda), Sicilia(tm) 250, 350, 550, 770, 256, 256N, 358 (Fuji Silicia Chemical Co.), SILDEX(tm) H-31, H-32, H-51, H-52, H-121, H-122, L-31, L-51, L-121 (Asahi Glass Co., 30 Ltd.), Atopearl(tm) C, CM, HL, MT, A, G (Negami Industry Co., Ltd.), LANCO WAX(tm) P P-1362D, CP-1481F, PE-1500F, TF-1780, P EW-155, D25 (Ito Oil Co.), Techpolymer(tm) MB, MBX, SBX, EAX, MBP, SBP, MB-S, MB-SS, SB-S, MBTP (Sekisui Plastics Co., Ltd.), Epost r(tm) L15, MS, M30, S12, S6, S

(Nippon Shokubai Kagaku Kogyo Co., Ltd.), HIGH FLAT(tm) 2356, X23, 31 (Gifu Serack Co., Ltd.), and MA-07, A-30, B-15, KF-5, KF-6, KF-14, MA-100, MA-101 (Koyo Kagaku Co., Ltd.). These glossing preventives have an average particle 5 diameter of 0.5 to 50 μm , preferably 1 to 20 μm . If the average particle size is less than 0.5 μm , no glossing preventive effects can be exhibited; if more than 50 μm , surface smoothness of the product is reduced. The glossing preventives can be added in an amount less than 10 10 by weight, preferably less than 10% by weight, in the composition of the present invention. Strength of the coating film may be decreased, if the amount of the glossing preventives is greater than 20% by weight. Among the above glossing preventives, inorganic glossing 15 preventives such as wet silica, dry silica, magnesium carbonate, and talc are preferred.

The composition of the present invention may be used diluted with a solvent. Preferred solvents are n-hexane, cyclohexane, toluene, xylene, methanol, ethanol, 20 iso-propyl alcohol, 1-buthanol, 2-buthanol, iso-butyl alcohol, iso-pentyl alcohol, cyclohexanol, methyl cyclohexanol, methyl acetate, ethyl acetate, propyl acetate, iso-propyl acetate, butyl acetate, pentyl acetate, iso-pentyl acetate, methyl propionate, ethyl propionate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, diethyl oxalate, dibutyl oxalate, diethyl malonate, methyl lactate, ethyl lactate, propyl lactate, butyl lactate, dioxane, tetrahydrofuran, acetone, 30 methyl ethyl ketone, methyl butyl ketone, methyl iso-butyl ketone, cyclohexanone, methyl cyclohexanone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate,

propylene glycol monoethyl ether acetate, and ethylene glycol monobutyl ether acetate.

The composition of the present invention has a viscosity preferably of 10 to 10,000 mPa.s, and more 5 preferably 50 to 5,000 mPa.s.

The composition of the present invention is preferably cured by radiation. When the photopolymerization initiator which is optionally added as the component (D) is not used, the composition should be 10 cured by radiation such as X-rays, electron beams, α -rays, β -rays, or γ -rays, preferably by electron beams. When the photopolymerization initiator is added, the composition is cured by radiation such as visible lights, ultraviolet lights, X-rays, electron beams, α -rays, β -rays, or γ -rays, preferably by ultraviolet lights. 15

Ultraviolet lights are irradiated at a dose preferably of 1 to 10,000 mJ/cm². When electron beams are used to cure the composition, a dose of 0.1 to 10 Mrad is preferably applied.

20 Irradiation is preferably carried out using a conveyer irradiation device.

EXAMPLES

The present invention will be hereinafter described in 25 more detail by way of examples which are given for illustration of the present invention and shall not to be construed as limiting the present invention.

Synthesis of urethane acrylate A1

30 278 g (1.25 mol) of 3-isocyanatemethyl-3,5,5-trimethylcyclohexyl isocyanate, 0.2 g of 2,6-di-tert-butyl-4-methylphenol, as a polymerization inhibitor, and 0.8 g dibutyltin dilaurate, as a catalyst, were placed in a reaction vessel equipped

with a stirrer. The mixture was cooled with ice to 10°C and 183 g (1.58 mol) of 2-hydroxyethyl acrylate was added while controlling the temperature below 20°C. After the addition, the mixture was stirred for one hour at 10-20°C.

5 Then, 57 g (0.057 mol) of polytetramethylene glycol having a number average molecular weight of 1,000 (PTGL1000(tm) manufactured by Hodogaya Chemical Co., Ltd.) was added while controlling the temperature below 50°C. Next, 74 g (0.27 mol) of trimethylolpropane ethylene oxide addition

10 triol having a number average molecular weight of 271 (TMP30(tm), manufactured by Nippon Emulsion Co., Ltd.) was added while controlling the temperature below 50°C. After the addition, the mixture was stirred for five hours while controlling the temperature at 50-60°C before terminating

15 the reaction, thus obtaining urethane acrylate A1.

Synthesis of urethane acrylate A2

236 g (1.25 mol) of 1,3-bis(isocyanatemethyl)cyclohexane, 0.24 g of 2,6-di-tert-butyl-4-methylphenol, as a polymerization inhibitor, and 0.8 g dibutyltin dilaurate, as a catalyst, were placed in a reaction vessel equipped with a stirrer. The mixture was cooled with ice to 10°C and 164 g (1.41 mol) of 2-hydroxyethyl acrylate was added while controlling the temperature below 20°C. After the addition, the mixture was stirred for one hour at 10-20°C.

25 Then, 57 g (0.05 mol) of polycarbonate diol having a number average molecular weight of 1,000 (PNOC1000(tm) manufactured by Kuraray Co., Ltd.) was added while controlling the temperature below 50°C. Next, 89 g (0.33 mol) of trimethylolpropane ethylene oxide addition triol having a number average molecular weight of 271 (TMP30(tm), manufactured by Nippon Emulsion Co., Ltd.) was added while controlling the temperature below 50°C. After

the addition, the mixture was stirred for five hours while controlling the temperature at 50-60°C before terminating the reaction, thus obtaining urethane acrylate A2.

5 Examples and Comparative Examples

Preparation of compositions for forming coating films

The following components were charged into a reaction vessel equipped with a stirrer at proportions listed in Table 1 and blended to obtain the compositions 10 for forming coating films of Examples 1 to 8 and Comparative Examples 1 to 4.

Component (A)

A1: Urethane acrylate A1

A2: Urethane acrylate A2

15 Component (B)

B1: 2-Acryloyloxyethyl succinate (NK Ester^(tm)), manufactured by Shin-Nakamura Chemical Co.)

B2: Tripropylene glycol diacrylate (APG-200^(tm)), manufactured by Shin-Nakamura Chemical Co.)

B3: Ethoxyethoxyethyl acrylate (Viscoat^(tm) 190, manufactured by Osaka Organic Chemical Industry, Ltd.)

B4: Acryloylmorpholine (ACMO^(tm)), manufactured by Kojin Co., Ltd.)

B5: Phenoxyethyl acrylate (NK Ester AMP-10G^(tm)), manufactured by Shin-Nakamura Chemical Co.)

B6: 2,2-bis[4-(Acryloxydiethoxy)phenyl]propane (Viscoat^(tm) 700, manufactured by Osaka Organic Chemical Industry, Ltd.)

B7: Hydroxy pivalic acid neopentyl diacrylate (KAYARAD MANDA^(tm)), manufactured by Nippon Kayaku Co., Ltd.)

Component (C)

5 C1: Fine powder of phosphosilicate glass containing silver ion (Ionpure WPA(tm), manufactured by Ishizuka Glass Co.)

 C2: Fine powder of borosilicate glass containing silver ion (Ionpure IP(tm), manufactured by Ishizuka Glass Co.)

Component (D)

10 D1: 1-Hydroxycyclohexyl phenyl ketone (Irgacure(tm), manufactured by Ciba Geigy)

 D2: Benzophenone

 D3: Methylbenzoyl formate (Bicure 55(tm), manufactured by AKZO)

15 D4: 2-Hydroxy-2-methyl-1-phenylpropan-1-one (Darocur(tm) 1173, manufactured by Merck Co.)

Component (E)

20 E1: α -[2-(4-chlorophenyl)-ethyl]- α -(1,1-dimethylethyl)-1H-1,2,4-triazol-1-yl -ethanol

 E2: Zeolite containing silver ion (containing 3 wt% of Ag₂O and 15 wt% of ZnO)

 E3: Calcium hydroxide containing zinc ion (Ca_{0.9}Zn_{0.1}(OH)₂)

25 E4: N-Fluorodichloromethylthiophthalimide

Component (F)

 F1: TINUVIN400(tm), manufactured by Ciba Geigy

Other Component

30 G1: Fine powder of silica (Nipseal(tm) SS-50, manufactured by Nippon Silica Co.)

TABLE 1

- 32 -

Component	Example							
	1	2	3	4	5	6	7	8
F1								0.2
G1	5	4.9	4.9	4.8	5	5	5	5

TABLE 2

5

Component	Comparative Example			
	1	2	3	4
A1	34	33	33.3	33.7
A2				
B1	12.2	11.8	11.9	12.1
B2	18.2	17.8	17.9	18.1
B3	12.2	11.8	11.9	12.1
B4	6.6	6.4	6.5	6.5
B5				
B6				
B7	6.6	6.4	6.5	6.5
C1				
C2				
D1	5.1	4.9	5	5
D2				
D3				
D4				

		Comparative Example		
Component	1	2	3	4
E1				
E2		3		
E4			2	
E4				1
5 F1				
G1	5.1	4.9	5	5

Degree of yellowing by UV lights(color difference),
 10 adhesion property to substrates, light resistance, heat
 resistance, antibacterial characteristics, and antifungal
 characteristics of the compositions prepared above
 (Examples 1 to 8 and Comparative Examples 1 to 4) were
 examined according to the following methods.

15 <Measurement of color differences>

Preparation of samples:

The composition to be tested was applied to a
 flat, smooth glass plate using an applicator bar 15MIL(tm)
 (manufactured by Kumagairiki Kogyo) and irradiated by UV
 20 light at 1 J/cm² using a conveyer UV irradiation device
 equipped with a metal halide lamp (manufactured by Eye
 Graphics Co.). The cured composition was peeled off from
 the glass plate to obtain a cured film with a thickness of
 about 200 μ m. An eye UV light integrating meter
 25 UVPF-36(tm) (manufactured by was used Eye Graphics Co.)
 was used for the measurement of irradiated UV light
 energy.

Measurement of color difference:

Color difference (ΔE) from a standard white board was measured using a color difference meter CR-300(tm) (manufactured by Minolta Camera Co., Ltd.)

<Measurement of adhesion property>

5 Preparation of samples:

The composition was applied to a hard polyvinyl chloride board using a bar coater #10, followed by irradiation of UV light at 0.5 J/cm^2 from a conveyer UV irradiation device equipped with a mercury lamp (manufactured by Oak Manufacturing Co.) to obtain a cured film with a thickness of $15 \mu\text{m}$. The adhesion property was measured by the cross-cut adhesion test according to JIS K5400. The adhesion was indicated by the number of $1 \text{ mm} \times 1 \text{ mm}$ squares left unpeeled among 100 squares.

15 <Light resistance>

The samples used for the color difference test and the cross-cut adhesion test were irradiated by UV light from 8 QVA351(tm) lamps installed in the V-acceleration weathering tester (manufactured by Q-Panel Co., Ltd.). Color difference after 120 hours and the adhesion after 1000 hours were measured.

<Heat resistance>

The samples for the color difference test and the cross-cut adhesion test were placed in an oven at 80°C to measure the color difference after 120 hours and the adhesion after 1000 hours.

<Test for antibacterial characteristics>

The composition was applied to a soft polyvinyl chloride board using a bar coater to produce a film with a thickness of about $30 \mu\text{m}$, followed by irradiation of UV light at 0.5 J/cm^2 from a conveyer UV irradiation device equipped with a mercury lamp (manufactured by Oak Manufacturing Co.) to obtain a cured film with a thickness of about $30 \mu\text{m}$. The UV light irradiation energy was

measured by ORC UV light luminometer UV-350(tm) (manufactured by Oak Manufacturing Co.). The film was cut into pieces of 5 cm x 5 cm. A bacterial solution containing about 10⁶ cells/ml was applied to the test 5 piece, which was allowed to stand at 35°C for 24 hours. The bacterial solution on the test piece was washed out to count the number of living cells by microscope. As a control, the same quantity of the bacterial solution as applied to the test piece was applied to a petri dish and 10 allowed to stand 35°C for 24 hours, to count the number of living cells in the same manner.

E-coli and yellow staphylococcus were independently used as the test microorganisms.

<Antifungal test>

15 Black mold (Aspergillus niger) and blue mold (Penicillium funicolosum), Chaetomium globosum, Gliocladium virens, and Aureobasidium pullulans were used for the test.

Cell suspensions, each containing a single 20 cell-line in an amount of 1,000,000 to 200,000 cells per liter, were prepared using an inorganic base solution containing 0.7 g/l of KH_2PO_4 , 0.7 g/l of K_2HPO_4 , 0.7 g/l of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 1.0 g/l of NH_4NO_3 , 0.05 g/l of NaCl , 0.002 g/l of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.002 g/l of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and 0.002 g/l of 25 $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$. A mixed cell line suspension was prepared by blending equivalent quantities of the single cell line suspensions. The same test pieces used for the test for the antibacterial characteristics were placed in an inorganic agar medium prepared by solidifying the above 30 inorganic base solution with the addition of 1.5% of agar. The mixed cell line suspension was sprayed over the test pieces and cells were grown at 28-30°C, RH 85% for 14 days. The growth of molds produced on the surface of the test pieces was microscopically observed to evaluate the

growth of molds according to ASTM-G21. The results are indicated according the criteria shown in Table 3. The results of the evaluations of antibacterial characteristics, antifungal characteristics, light resistance, and heat resistance are shown in Tables 4 and 5.

TABLE 3

10

	Classification	Description
	0	No fungi production was observed.
15	1	Slight fungi production (10% or less on the surface of the test piece) was observed.
	2	Some fungi production (10 to 30% on the surface of the test piece) was observed.
	3	Fungi production was significant (30 to 60% on the surface of the test piece).
20	4	Fungi production was remarkable (over 60% on the surface of the test piece).

25

TABLE 4

		Example							
		1	2	3	4	5	6	7	8
5	Light resistance								
	ΔE								
	QUV Not irradiated	3.2	3.0	2.9	3.0	3.0	3.0	3.0	3.0
	QUV After 120 hours	8.0	8.2	7.0	6.5	7.5	9.0	8.5	7.0
10	Adhesion								
	QUV Not irradiated	100	100	100	100	100	100	100	100
	QUV After 1000 hours	100	100	100	100	100	100	100	100
15	Heat resistance								
	ΔE								
	Before heating	3.2	3.0	2.9	3.0	3.0	3.0	3.0	3.0
	80°C, 120 hours	5.6	5.9	6.3	5.4	7.4	8.5	6.0	7.6
	Adhesion								
	Before heating	100	100	100	100	100	100	100	100
	80°C, 1000 hours	100	100	100	100	100	100	100	100

Antibacterial characteristics		E. coli		After 0 hour		After 24 hours		yellow staphylococcus		After 0 hour		After 24 hours		Antifungal characteristics		After 14 days	
4x10 ⁵	4x10 ⁵	2x10 ⁴	4x10 ⁴	1x10 ⁵	1x10 ⁵	4x10 ⁴	4x10 ⁵	9x10 ⁵	8x10 ⁵	2x10 ⁴	2x10 ⁵	9x10 ⁵	9x10 ⁵	1	1	1	
<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	

TABLE 5

		Comparative Example			
		1	2	3	4
5	Light resistance				
	ΔE				
	QUV Not irradiated	3.0	3.2	3.1	2.9
	QUV After 120 hours	8.0	15.4	7.5	16.0
10	Adhesion				
	QUV Not irradiated	100	100	100	100
	QUV After 1,000 hours	100	60	100	0
15	Heat resistance				
	ΔE				
	Before heating	3.0	3.2	3.1	2.9
	80°C, 120 hours	6.0	10.5	5.5	6.7
20	Adhesion				
	Before heating	100	100	100	100
	80°C, 1,000 hours	100	54	100	0
25	Antibacterial characteristics				
	E. coli				
	After 0 hour	1×10^5	1×10^5	4×10^5	4×10^5
	After 24 hours	9×10^3	60	40	1×10^4
	yellow staphylococcus				
	After 0 hour	9×10^5	9×10^5	9×10^5	9×10^5
	After 24 hours	6×10^5	40	60	2×10^3
30	Antifungal characteristics				
	After 14 days	4	3	3	4

- 40 -

The composition for forming coating films of the present invention has superior antibacterial and antifungal activities, is free from yellowing due to lights and heat, and exhibits excellent adhesion to 5 various materials such as plastics, woods, papers, clothes, metals, and ceramics.

WHAT IS CLAIMED IS:

1. A composition for forming coating films comprising:
 - (A) a urethane (meth)acrylate obtained by reacting a polyol (a) having 2 to 6 hydroxyl groups in a molecule, a diisocyanate, and a (meth)acrylate having a hydroxyl group;
 - (B) a reactive diluent and
 - (C) fine powder of glass containing silver ion as an antibacterial agent.
- 10 2. The composition according to claim 1, further comprising one or more components selected from the group consisting of:
 - (D) a radiation polymerization initiator,
 - (E) an antibacterial agent other than the component (C), and
 - (F) a ultraviolet absorber.
- 15 3. The composition according to any one of claims 1-2, wherein the reactive diluent (B) is a (meth)acrylate containing at least one (meth)acryloyl group in a molecule.
- 20 4. The composition according to any one of claims 1-3, wherein the polyol (a) is a polyether polyol; a polyester polyol, a polycarbonate polyol or a polycarbonate polyol.
- 25 5. The composition according to any one of claims 1-4, wherein the number average molecular weight of the polyol (a) is in the range of 50 to 15,000.
- 30 6. The composition according to any one of claims 1-5, wherein the weight average molecular weight of the urethane (meth)acrylate (A) is 400 to 20,000.
- 35 7. The composition according to any one of claims 1-6, wherein the amount of urethane acrylate is 5-60% by weight [calculated on the total composition].

8. The composition according to any one of claims 1-7, wherein the reactive diluent (B) is present in an amount of 30-90 wt.% [calculated on the total composition].
- 5 9. The composition according to any one of claims 1-8, wherein the glass of component (C) is silicate glass, soda lime glass, borosilicate glass or phosphosilicate glass.
10. The composition according to any one of claims 1-9, wherein the glass contains 0.001 to 10 wt.% of silver ions.
11. The composition according to claim 10, wherein the glass contains 0.01 to 5 wt.% silver ions.
- 15 12. The composition according to any one of claims 1-11, wherein the compositing comprises 0.1-10 wt.% of glass containing silver ions (C).
13. The composition according to any one of claims 1-12, wherein the mean particle size of the glass containing silver ions is less than 50 μ m.
- 20 14. The composition according to any one of claims 1-13, wherein the radiation polymerization initiator is present in an amount of 1-10 wt.%.
15. The composition according to any one of claims 1-14, wherein the antibacterial agent other than component (C) is present in an amount of 0.1-3 wt.%.
- 25 16. The composition according to anyone of claims 1-15 wherein the composition further comprises an antifungal agent.
- 30 17. The composition according to any one of claims 1-16 wherein the composition has a viscosity of 10-10,000 mPa.s (at 25°C).
18. Cured coating obtained by radiation curing of a coating composition according to any one of claims 35 1-17.

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/NL 97/00318

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D5/14 C09D175/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 19415 A (BORDEN UK LTD ;ALGAR BRIAN (GB)) 1 September 1994 see abstract; claims see page 6, line 14 - page 7, line 11 ---	1,18
Y	DATABASE WPI Section Ch, Week 9123 Derwent Publications Ltd., London, GB; Class A82, AN 91-169155 XP002041610 & JP 03 103 481 A (IWAHASHI S) , 30 April 1991 see abstract ---	1-18
Y	EP 0 046 354 A (SCOTT BADER CO) 24 February 1982 see claims; example 6 ---	1-18

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- *'P' document published prior to the international filing date but later than the priority date claimed

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*'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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1

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 97/00318

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 992 524 A (COADY CLIVE J ET AL) 12 February 1991 see abstract; claims -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

PCT/NL 97/00318

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